



Biobased nanocomposites from clay modified blend of epoxidized soybean oil and cyanate ester resin



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ABSTRACT

Novel bio-based nanocomposites were prepared by blending surface modified natural clay with epoxidized soybean oil (ESO) and cyanate ester resin (CE). A convenient method was employed to modify the attapulgite (ATT) clay by adsorbing the poly(ethylene glycol) diglycidyl ether (PEGDE) onto the clay surface, which was confirmed by the appearance of a new peak of infrared spectroscopy due to hydrogen bonding and chelation. Thermogravimetric analysis (TGA) showed that the amount of PEGDE adsorbed on ATT was influenced by PEGDE concentration in acetone solution. Scanning electron microscope (SEM) and transmission electron microscope (TEM) results showed that nanoscaled ATT dispersed well in the blend of epoxidized soybean oil (ESO) before and after curing. The thermal-physical and mechanical properties were evaluated by dynamic mechanical analysis (DMA), TGA and tensile mechanical test. The nanocomposites showed higher glass transition temperature and modulus, and the tensile strength of the nanocomposites was reinforced as compared to that of ESO/CE blends.

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1. Introduction

Vegetable oil, as the cheapest and most abundant biological feedstock, has been studied extensively in recent years for composites and coating materials because of its advantages such as low toxicity and inherent biodegradability [1–4]. With systematic study, for example, Mohanty et al. [5–7] investigated the epoxidized linseed oil based epoxy materials; Adekunle et al. [8] and Mustata et al. [9] tested the performance of soybean oil composites, it is found that these renewable polymers could serve as an alternative to the traditional petroleum-based polymers through innovative design, because these novel bio-based polymers could be more cost-effective and eco-friendly than the existing petroleum-based polymers.

When bio-based polymers are used to replace part of the highly crosslinked thermosetting resins, the toughness of modified blend is usually increased. However, the modulus, tensile strength and thermal stability are decreased at the same time [10], which limited the application of these polymers in composites and coatings.

To solve this problem, one of the convenient ways without sacrificing eco-friendliness is organic–inorganic nanocompositing technique. Previously, many inorganic nanoparticles have been applied to modify polymer systems [11–14], such as layered silicates [15], TiO₂ [16], ZnO [17] and rod-like silicates [18], which

increased the mechanical properties of the composites due to their intrinsic properties.

However, the large specific surface of nanoparticles always results in aggregation, and their polar surface leads to poor compatibility with polymer matrices [19]. As a result, it's difficult to prepare nanocomposites with well dispersed nanoparticles via simple mixing. Therefore, nanoparticles are surface modified to improve their dispersibility. For example, Chen et al. [20] studied the organically modified oxidized multi-walled carbon nanotubes, and found that they can be well dispersed in epoxy matrix and improved thermo-mechanical performance of the material; Wang et al. [21] found that the surface modified TiO₂ had a finer dispersion and better compatibility than bare TiO₂; Fu et al. [22] investigated the organically modified clay with polyhedral oligomeric silsesquioxane (POSS).

The natural clay attapulgite (ATT) belongs to a family of hydrated magnesium silicates with a fibrous structure of approximately 20 nm in diameter and several micrometers in length scale, which gives ATT larger surface area and stronger absorptive capacity than those of any other natural minerals [23]. These properties, as well as good mechanical strength and thermal stability, make ATT an ideal candidate to reinforce polymeric materials. However, ATT has not received much attention in the application of thermosets even though Nutt et al. [24] found that ATT could improve the mechanical properties and dimensional stability of epoxy resins significantly. Although some procedures have been developed to modify the ATT [24–26], it is still necessary to explore some methods more convenient and practical for the actual application.

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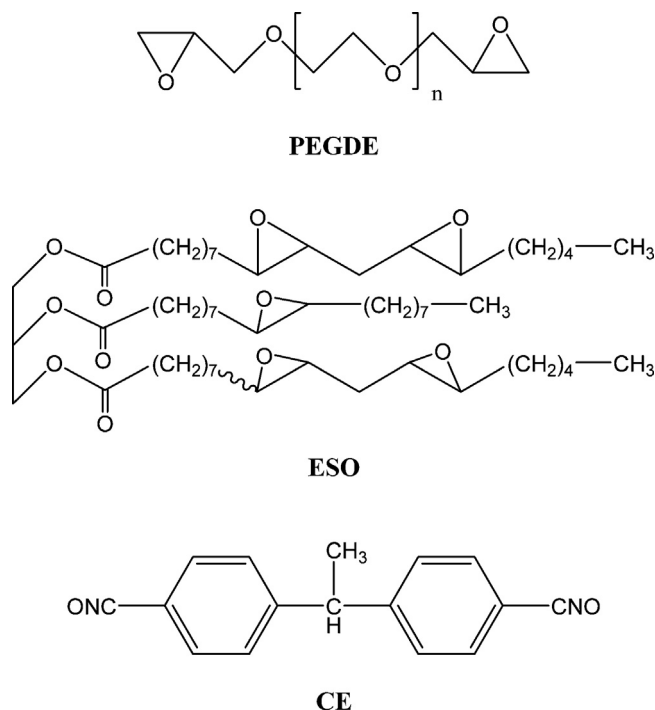


Fig. 1. Chemical structures of poly(ethylene glycol) diglycidyl ether (PEGDE), epoxidized soybean oil (ESO) and cyanate ester resin (CE).

Recently, poly(ethylene oxide) (PEO) has been applied as a modifier for layered nanoparticles due to its interactions with metal ions, e.g. Tunney et al. [27] obtained high performance aluminosilicate nanocomposites with PEO surface-modified kaolinite. This arouses our interest in the modification of ATT by PEO for the preparation of new bio-based materials.

In our previous works, cyanate ester resin, a widely applied coating and structural material in microelectronic industry, was modified by epoxidized soybean oil (ESO), which improved the toughness of cyanate significantly and lowered down the water sorption at the same time, while this modification further made the material more cost-effective and environment friendly [28]. The blend was then reinforced by in situ generated nano-silica [29] to compensate the drop in thermal and modulus due to the introduction of ESO, however, this in situ generation method was tedious and required well controlled hydrolysis process.

As a result, in this study, a convenient PEO surface modification method was applied for ATT to improve its compatibility with the bio-based cyanate materials; while the PEO was further functionalized with epoxy group (PEGDE) to improve its interaction with resin matrix. The effect of PEGDE concentration and ATT contents on the thermal and mechanical properties of composites was investigated in this article.

2. Experimental

2.1. Materials and sample preparation

The cyanate ester resin (CE), 1,1'-bis(4-cyanatophenyl) ethane, with a cyanate equivalent of 132 g/eq was obtained from Shanghai Huifeng Technical & Business Co. (Shanghai, China). Epoxidized soybean oil (ESO) (oxirane content as 6.8%) was obtained from Shanghai Tongxin Chemical Auxiliary Plant (Shanghai, China). Poly(ethylene glycol) diglycidyl ether (PEGDE) as an oligomer of 10 units and $M_n \approx 526$ was received from Aldrich Co. The chemical structures of PEGDE, ESO and CE resin are shown in Fig. 1. Attapulgit (ATT) nano-rods (Attagel 50) were provided by Engelhard

Table 1

Name and composition of the samples studied (PEGDE and ATT concentration) for the different formulations.

Composition	Concentration (%)	
	PEGDE ^a	ATT
CES-blend	0	0
CES-PEGDE	0.5 ^b	0
CES-none-2	0	2
CES-1 ppm-2	0.001	2
CES-10 ppm-2	0.01	2
CES-100 ppm-2	0.1	2
CES-1%-2	1	2
CES-100 ppm-1	0.1	1
CES-100 ppm-3	0.1	3
CES-100 ppm-4	0.1	4

^a The concentration of PEGDE in acetone solution.

^b The concentration of PEGDE in resin blend. The weight ratio of cyanate to epoxidized soybean oil is 80:20.

Co., United States. Copper (II) acetylacetonate and nonylphenol were provided by Sigma–Aldrich.

Attapulgit was baked in muffle furnace at 500 °C for 6 h before modification. For surface modification, ATT was first dispersed in acetone with 1 wt%, and then different amounts of PEGDE were added, the suspensions were stirred vigorously for 6 h and sonicated for 2 h at room temperature. The suspensions were filtered and washed with acetone for three times, and then the obtained white powders were dried in vacuum at 60 °C for 24 h.

The blend of CE and ESO in a weight ratio of 80:20 was selected due to its best performance as compared with other ones in both toughness and water sorption [28] and prepared by the procedure we have reported previously. The modified ATT was dispersed into the blend with vigorous stirring and ultrasonication for 1 h. Then the modified blends were cured with copper (II) acetylacetonate as a catalyst and nonylphenol as a co-catalyst at 177 °C for 2 h, and postcured at 210 °C for 2 h. The weight ratio of the CE-ESO/catalyst/co-catalyst was 100/0.05/2. The samples were designated as Table 1, where CES means CE-ESO blend.

2.2. Measurement

Fourier transform infrared spectroscopy (FTIR) was performed at ambient temperature with a Thermo Nicolet Nexus 440 Spectrometer, 4 cm⁻¹ resolution and 32 scans were used.

Thermal gravimetric analysis were performed with a Pyris 1 TGA equipment (Perkin Elmer Inc, USA) under air flow of 40 ml/min. The heating rate is 10 °C/min and the temperature range was from 50 °C to 800 °C.

The curing conversions and reaction rates were determined by Perkin-Elmer differential scanning calorimeter (DSC, Pyris 1). The samples were isothermally cured at 177 °C under a nitrogen flow of 20 ml/min. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 5–10 mg.

The melt viscosity variations of the composites during curing reaction were recorded with an ARES-4A rheometer (TA Instrument, USA). The samples were tested under a parallel plate mode and a controlled strain of 1% to ensure that the measurements were performed under linear viscoelastic conditions.

The morphologies of the fully cured samples were observed by scanning electron microscope (SEM, Tescan TS5163MM). The samples were fractured in liquid nitrogen and coated with a fine gold layer before observation.

The dynamic mechanical properties were performed with a Netzsch dynamic mechanical analysis (DMA 242) operating in the single cantilever mode at an oscillation frequency of 1.0 Hz. The

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